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Identification and evaluation of fundamental transport and transformation process models.

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Abstract

Chemical fate models require explicit algorithms for computing the effects of transformation and transport processes on the spatial and temporal distribution of chemical concentrations. Transport processes in aquatic systems are driven by physical characteristics of the system, and include hydrodynamic transport, sorption/desorption, sediment transport, exchanges between bed sediments and the overlying water column, and volatilization/absorption across the atmosphere/water interface. Chemical transformations include direct and indirect photolysis, hydrolytic reactions, and reductions. Biological processes include microbial and algal transformations, and biological transport vectors. This paper gives a brief evaluation of the current status of knowledge in each of these areas, indications of the chemical and environmental parameters needed for quantitative descriptions of the process kinetics, and suggestions for further research.

Introduction

Mathematical models designed to evaluate the behavior of chemicals in aquatic environments must include descriptions of the physical, chemical, and biological processes governing the transport and fate of compounds. In order to be fully general, and therefore useful in a wide range of applications, these process models should be constructed as a combination of properties of the chemical and as functions of independently measurable environmental driving forces. This "second-order" or "system-independent" approach makes it possible to study the fundamental chemistry of compounds in the laboratory and then, based on independent studies of the levels of driving forces in aquatic systems, evaluate the probable behavior of the compound in systems that have never been exposed to it (Baughman and Burns 1980).

This approach depends for its success on the development of a thorough understanding of transport and transformation processes, with a secure base in fundamental theory and physical causation. It requires that the process chemist adopt an especially sophisticated and subtle experimental approach, for in general the reaction conditions and chemical concentrations in environmental situations are inconveniently benign, rendering process chemistry inordinately difficult -- reactions are slow, extreme analytical precision is required to trace the time-course of reactions, reaction conditions must be rigorously

characterized, and a mass balance often must be maintained to confirm the integrity of the experiment.

It is sometimes plausibly argued that coarser studies can serve to delineate the dominant fate processes of chemicals and that minor and slow pathways have little effect on the outcome of environmental evaluations. Although this argument has some merit, it also has several flaws. For one thing, the behavior of synthetic chemicals can undergo significant qualitative changes when the chemical is present at high concentrations. Thus, although the behavior of synthetic chemicals at high concentrations is of interest for evaluating chemical spills, accidents, and waste depositories, at the dispersed concentrations more typical of aquatic systems such studies can exaggerate the speed of transformation and degradation of dilute residuals.

Secondly, the next generation of exposure models will include the production of secondary "daughter" products via transformations occurring in the environment; the possibility of production of secondary compounds of high toxicity will force attention on the kinetics of these transformation pathways even when they are relatively slow and of little importance (in a mass-balance sense) to the overall fate of the parent compound. Finally, it should be remarked that when a slow transformation pathway is the only process that degrades a chemical in the

environment, slowness cannot be equated with insignificance if we wish to estimate the persistence of the compound in the global environment.

This paper outlines the current state of knowledge of those aspects of transformation and transport processes required for inclusion in environmental models. It includes a brief description of many of the characteristic formulations current in the literature, some discussion of the environmental information required to bring them to bear on environmental situations, and some exploration of areas of ambiguity and opportunities for further research.

Physical Processes

Physical processes include hydrodynamic transport, capture of synthetic chemicals by solid phases (sorption and its kinetics), transport of solid phases containing sorbed chemicals, transport across the benthic boundary layer, and volatilization (and absorption) across the air/water interface.

1. Hydrodynamic Transport. Turbulent and advective water motions in aquatic systems have been studied for many years. The temporal and spatial scales of these studies are very diverse, ranging from the behavior of effluent streams to overall characterizations of mean circulation patterns in large lakes and the oceans. A thorough exploration of this vast body of material

is far beyond the scope of this discussion; suffice it to say that hydrodynamic flows carry an entrained load of dissolved materials and that, when these dissolved materials include synthetic compounds, the transport of the chemicals can be readily derived by regarding the flow as a simple carrier. In many instances a model for synthetic chemicals can be "piggy-backed" on either a hydrodynamic transport model or on a transport description derived from observational data; this strategy is not uncommon in generalized water quality models.

The study of hydrodynamics is best developed for rivers (Shen 1979), estuaries (Nihoul 1978), and flowing water systems in general. Although the hydromechanics of ponds and lakes has not been totally neglected (e.g., Gibbs 1977) and some lakes have received fairly intensive study (e.g., Li 1973), vertical transport in stratified water bodies continues to pose difficulties for general models. Transport across the thermocline is dominated in many instances by episodic events, including wind-induced eddies, storm surges, and internal seiches (Wetzel 1975). In some studies, these transport events have been successfully described via a summary overall dispersion coefficient (e.g., Snodgrass 1977), that is, by analogy with Fickian diffusion. This approach may ultimately be supplemented with a stochastic description based on mixing events. Significant differences in predicted chemical residuals can be envisioned, for example, from rapid photolysis of chemicals

episodically injected into sunlit surface waters from a (relatively dark) hypolimnion. This possibility clearly exists, but evaluation of its potential significance for exposure modeling must await comparisons between the results of appropriate alternative whole-system models.

2. Sorption. The capture of neutral organic compounds by non-living sedimentary materials is a strong function of the organic carbon content of the solid phases (Karickhoff, Brown, and Scott 1979). Equilibrium sorption of these "hydrophobic" compounds has been successfully described via a carbon-normalized partition coefficient on both a whole-sediment basis and by particle size classes. The success of the whole-sediment approach for natural sediments apparently derives from the fact that most naturally occurring sediment organic matter falls in the "silt" or "fine" particle size fractions. So long as the dissolved concentration of the sorbing compound does not exceed 1.E-05 M, a linear isotherm (i.e. a partition coefficient) can be used to describe the phenomenon. At higher concentrations, the capacity of the solid to accept additional compound can be exceeded, and a nonlinear Freundlich or Langmuir isotherm must be invoked. One recent study (O'Connor and Connolly 1981) suggests that partition coefficients may decrease under large sediment/water ratios. If this result represents a general phenomenon, it will require careful additional study in order to derive a system-independent characterization and a causal

explanation of the effect.

The "bound residue" phenomenon, with its implicit sediment desorption hysteresis, is a subject of particular concern for environmental models. Karickhoff (1980) has proposed a two-step sorption model that may encompass most experimental observations of "bound residues." This model suggests that sorption is composed of a labile pool in continuous equilibrium with dissolved chemical, plus a more slowly exchanging pool that may reside in interior zones of the solid phases. The rate of release of sorbed compound from the refractory pool is inversely correlated with the overall partition coefficient of the compound, with desorption halflives in some cases approaching 40 days.

This approach has several implications for environmental models. In the case of reactive compounds (i.e., compounds with short (<10--40 day) free-water halflives), desorption kinetics can become a rate-limiting step in the overall degradation of the compound in some circumstances. This phenomenon is likely to be of considerable importance in the description of transformation reactions in bottom sediments, because slow desorption halflives occur primarily for extensively sorbed compounds, which tend to be captured by benthic subsystems. On the other hand, a finite release time for sorbed chemicals simplifies the computation of volatilization rates. Because the residence time of sorbing

particles in the air/water interface zone is very short, the computation of dissolved, unionized species (subject to volatilization) near the air/water interface can be simply based on conditions in the bulk phase of the water column.

Sorption of ionizable compounds (organic acids and bases) has yet to be described in a fully system-independent fashion. Ionization itself is quite fast and can be readily described via an equilibrium approach using the pH of the water-body and chemical ionization constants (pKa, pKb). The sorption of the resulting ions involves competition with normal inorganic and organic cations and anions. Sorption of organic cations can be described fairly well via a competitive Langmuir isotherm, using cation exchange capacity (CEC) as a general capacity factor. In this approach, the (compound-specific) parameters of the isotherm are determined on a single sediment, and sorption to other sediments is estimated via sediment pH and CEC (Brown 1981). Increased precision could be achieved via a detailed characterization of the mineralogy and capacity of each particle size class, but the level of detailed environmental data required to implement such an approach in operational exposure models may be exceedingly difficult to attain.

Given partition coefficients for neutral and ionic species, computation of the (local) equilibrium distribution of a compound in a given segment of an aquatic system can be mechanized in a

straightforward way (Stumm and Morgan 1970, Burns et al. 1981). Nonlinear isotherms and detailed sorption kinetics have yet to be incorporated in operational exposure models, however.

One additional aspect of sorption phenomena deserves at least passing mention. The presence of dissolved organic matter (DOC) in a water sample has been observed to "solubilize" some hydrophobic compounds (e.g., Wershaw, Burcar, and Goldberg 1969). This phenomenon probably derives from the same hydrophobic mechanism driving sorption of neutral organics to solid phases, and the "solubilization" phenomenon has been successfully described via a simple partition coefficient (Perdue and Wolfe 1981). Given the dissolved organic carbon content of a water-body, it should be possible to describe the equilibrium association of hydrophobic compounds with DOC using conventional equilibrium partitioning methods.

3. Sediment Transport. Sediment transport, like hydrodynamic transport, has been of interest to the engineering profession for many years. Many comprehensive discussions of the dynamics of fluvial sediment transport have appeared in the literature (e.g., Simons and Senturk 1977, Garde and Ranga Raju 1977). As with hydrodynamic transport, one possible strategy for environmental modeling is to "piggy-back" the transport of sorbed synthetic chemicals on a model or description of transport of the sediment phase itself. The success of this strategy obviously

depends on the facility with which the distribution of the compound between sorbed and dissolved phases can be described. Because sediment transport dynamics are strongly dependent on particle sizes, this strategy requires careful treatment of particle-size dependencies of sorption. Models combining sediment and entrained chemical transport have already begun to appear (Onishi et al. 1980, Uchrin and Weber 1980).

In non-fluvial water bodies, interactions between benthic sediments and chemical contaminants often cannot simply be described via recourse to sediment transport dynamics. The simplest situation, and a fairly common one in most developed countries, occurs in run-of-the-river reservoirs. These systems are relatively impermanent landscape features because of their tendency to trap large quantities of river-borne sediments. The "trap efficiency" of reservoirs has been of interest to engineers for many years (e.g., Borland 1971), and in this special case the capture of fluvial sediments and burial of synthetic compounds in reservoir benthic systems can probably be described fairly well (e.g., Schnoor 1981).

4. Benthic Boundary Layer Transport. In many lakes and coastal seas, net sediment deposition can be very small. In these cases, capture of synthetic compounds may be driven primarily by the activities of the biota, which include physical disturbance by demersal fishes, irrigation of the sediments by

benthic macrofauna (Aller 1977), and sorption to surface layers followed by subduction and mixing of contaminated layers by crustacea and worm populations. In addition, physical stirring via sediment "bursting" (Heathershaw 1974, 1976) can facilitate exchange across the benthic interface. In general, transport across the benthic boundary layer can be described via an advection/dispersion equation (Berner 1980), in which the advection term is used to account for ground-water flow and the exchange events are described via a dispersion term.

The effect of benthic organisms on particle size fractionation is of particular concern in exposure modeling. Under typical conditions, lacustrine oligochaete populations can be active to a depth of about 10 to 15 cm in the sediment deposits (Jones and Bowser 1978). These organisms selectively ingest silts and fine particles and deposit a fecal layer on the surface of the sediment (Fisher 1979). Most sediment organic matter, and thus most synthetic organic contaminants, are associated with these particle sizes. These facts imply that burial of contaminated sediment fractions may be retarded by the activities of burrowing organisms under slowly depositing regimes. Vertical size fractionation, although an acknowledged phenomenon (Berner 1980), has not yet been explicitly incorporated into sediment transport or exposure models.

Estuarine systems are especially complex because of their

spatial mixture of fluvial, depositing, turbulent eroding, and stable sediment regimes. In the James estuary, net sedimentation rates vary from <1 to >19 cm/year; Kepone contamination accordingly varies from near-surface to burial at depths greater than 50 cm (Cutshall et al. 1981). Estuarine systems may afford significant research opportunites for testing alternative descriptions of exchange mechanisms across the benthic boundary layer in a wide variety of depositional regimes. The addition of sorption/desorption kinetics to sedimentation and benthic exchange models is a substantial research problem that thus far has received little attention.

5. Volatilization. The Whitman (1923) 2-film model for volatilization appears to work reasonably well for synthetic organic compounds. There are, however, at least six fairly distinct methods of computing transport resistance in the aqueous and gaseous phases of the air/water interface. In one of the initial applications of the Whitman model to environmental problems, Liss and Slater (1974) suggested that simple kinetic theory could be used to index chemical transport resistances to piston velocities of water vapor and the normal dissolved gases. This idea leads to use of the square root of the molecular weight of the volatilizing compound as a computational factor in the volatilization equations. A second method follows from a strict application of the formal logic of the Whitman model; in this method the diffusivity of the compound enters the equations as an

index factor. In a third approach, derivations based on renewal theory or penetration theory result in the use of the square root of diffusivities. Dobbins (1964) proposed a fourth approach that is a hybrid of film and renewal theory, in which the root of diffusivity used in the equations varies between 0.5 and 1.0 as a function of hydrodynamic turbulence. More recently, Mackay and coworkers (1980) have proposed the direct use of compound-specific Schmidt numbers (incorporating viscosity and diffusivity) to compute transport resistances, and Wolff and van der Heijde (1981) have proposed a method for estimating boundary-layer thicknesses, thereby arriving at transport resistances via molecular diffusion constants.

In some ways, then, we have a superabundance of similar volatilization models; the time is certainly ripe for comparative field tests of these approaches. The required chemical data include the Henry's Law constant, molecular weight, and diffusivity of the compound in air and water. (Some of these can be computed from other properties of the compound, e.g. computation of Henry's Law constant via vapor pressure and solubility (Mackay and Leinonen 1975).) Partition coefficients and ionization constants are also needed when effects of sorption and ionization are significant. Environmental data needed for these models include reaeration rates, windspeeds, temperature, and in some cases wind fetch and water current velocities.

The Whitman model has performed well in laboratory investigations. Because the flow fields in wind tunnels are much less turoulent than natural situations (Thibodeaux 1979), the most immediate need for field testing of volatilization models is perhaps for application of the models to compounds whose total transport resistance is controlled by the gas phase.

The 2-film approach has been regarded, in practice, as a method of computing average volatilization. Under these conditions, the Henry's Law constant of a compound can be used to estimate the percentage of the total transport resistance lying in each phase of the air/water interface (Mackay 1978). In the context of specific field validation sites, however, it should be remembered that strong diel shifts in transport resistance, and its distribution between phases, are possible. For example, volatilization of a compound that is nominally dominated by liquid-phase resistance could well be strongly retarded under very still atmospheric conditions (as can occur, for one case, in a small sheltered pond during nighttime hours), particularly if a shallow layer of stagnant contaminated air builds up over the surface of the water-body.

Chemical Processes

1. Direct Photolysis. Direct photolysis, in which direct absorption of sunlight by a synthetic chemical induces transformation of the compound, has been intensively studied and

incorporated into both process-specific (Zepp and Cline 1977) and more general (Burns et al. 1981) exposure models. The rate of sunlight absorption by the compound can be computed from the compound's absorption spectrum in pure water and sunlight intensity in a water-body. The efficiency of conversion of the compound to daughter products can be evaluated in the laboratory (Zepp 1978) and coupled to the compound's rate of light absorption in the environment to yield the process transformation rate.

Computation of rates of direct photolysis requires a knowledge of spectral solar intensity at depth in the water-body. These data can be computed via application of the Beer-Lambert law, from the solar spectrum at the surface of the water column; and the absorption spectra of chlorophylls, natural dissolved organics, suspended organic detritus and sediments, and light extinction via water itself. The chemical, and the environmental, data needed to compute rates of direct photolysis in the environment are both thus relatively easy to obtain.

Several research problems remain unresolved, however. The full effects of sorption on photolysis rates are imperfectly known. Surface sorption appears to accelerate immediate photolysis in some cases; this phenomenon may result from transfer of the chemical into a hydrocarbon-like microenvironment (Miller and Zepp 1979). In addition, the effects of multi-stage

sorption/desorption are not completely clear, although some experimental results can be rationalized via a 2-stage desorption model (Zepp and Schlotzhauer 1981). Although it has been hypothesized that inorganic species present at high concentrations in marine waters (e.g., chloride) may affect photolysis of organics, the possibility of such photonucleophilic reactions in marine waters has not been systematically investigated (Zepp and Baughman 1978).

Finally, some non-linear behaviors have been observed in direct photolysis studies but have yet to be installed in operational models. As a fairly trivial example, the contribution of a pollutant to the overall absorption spectrum of a water-body has generally been neglected; this phenomenon is probably important only for undiluted waste streams or heavily polluted systems. A less trivial example is the "quenching" of excited states of the chemical by dissolved oxygen. In practice this problem has been overcome by measuring reaction quantum yields in air-saturated water (Zepp 1980), but the rates of direct photolysis in oxygen-deficient sunlit waters (a presumably unusual condition) may be somewhat understated. Finally, some instances of photosensitization by a photoproduct have been described (e.g., Wagner, Kochevar, and Kemppainen 1972); the generality and environmental significance of this kind of nonlinearity has not been quantitatively addressed by either process chemists or by modelers.

2. Indirect Photolysis. Direct photolysis is not the sole pollutant transformation process driven by the solar flux in aquatic systems. The simultaneous occurrence of plant decomposition products ("humic materials"), dissolved oxygen, and sunlight often results in an acceleration of the rate of transformation of organic pollutants. Zepp and coworkers (1977a), for example, found that methoxychlor, with a direct photolysis halflife of more than 300 hours, had a halflife of as little as 2.2 hours under irradiation in natural waters containing dissolved humic materials. Further, Ross and Crosby (1975) found that a solution of aldrin in water from a taro paddy can be photochemically converted to dieldrin, despite the fact that aldrin does not absorb sunlight.

These kinds of reactions are usually termed "indirect" or "sensitized" photolysis. Indirect photolysis can be subdivided into two general classes of reactions. First, "sensitized photolysis" per se involves sunlight absorption and electronic excitation of a sensitizer (humic) molecule, followed by direct chemical interaction between the excited state of the sensitizer and a pollutant molecule. Possible chemical reactions include a direct energy transfer to the pollutant molecule, hydrogen atom transfer from pollutant to sensitizer to give free radicals, and union of sensitizer and pollutant yielding an excited-state complex or "exciplex" (Zepp and Baughman 1978). The resulting free radicals or exciplexes can then react with dissolved

molecular oxygen, a process termed "type I sensitized photooxidation" by these authors.

The second class of indirect photolysis involves the formation of chemical oxidants in natural waters, primarily via the interaction of sunlight, humic materials, and dissolved oxygen (type II sensitized photooxidation of Zepp and Baughman 1978). The primary oxidants known to occur in natural waters are hydroxyl and peroxy radicals (Mill, Hendry, and Richardson 1980) and singlet oxygen (Zepp et al. 1977b). Alkoxy radicals and diradicals may also contribute to environmental oxidation of some compounds, but their presence in natural waters has not been conclusively demonstrated (Mill 1980). Process mechanics and routes of transformation for one indirect pathway, photooxidation mediated by humic materials and singlet oxygen, have been described for air-saturated waters (Zepp, Baughman, and Schlotzhauer 1981a, 1981b; Zepp and Schlotzhauer 1981b). Much remains to be done, however, before a fully general treatment of indirect photochemical processes can be incorporated into routine exposure assessment models.

3. Hydrolysis. Hydrolysis of synthetic organic compounds also occurs via a variety of pathways. Specific-acid and -base catalyzed processes can be easily described in terms of the pH and temperature of water bodies (Wolfe 1980). Neutral hydrolysis (i.e., pH-independent mechanisms) can proceed either via direct

reactions involving the water molecule in the rate-limiting step, or via indirect molecular transformations involving water as a reactant. (Both are apparent first-order reactions in pure water solution.) The required chemical information can be encapsulated in a pH-rate profile (Fig. 1); hydrolysis kinetics are readily described via second-order equations incorporating the effects of temperature and, where required, ionization on chemical reactivity.

In general, sorption to sediment phases would be expected to retard the rate of chemical transformations requiring the presence of water. Sorption has been observed to retard reactions involving hydroxide or hydronium ion in the rate-limiting step (specific-acid and -base hydrolysis). Neutral reactions, however, appear to be unaffected by sorption, at least in sediment suspensions of up to 20 g/L, for a variety of neutral pathways (Wolfe oral comm.). This behavior may not hold in full benthic subsystems where the sediment/water ratio can be much greater than .02 kg/L, but the appropriate experimental investigations have not yet been accomplished. In addition, metal ion catalysis of hydrolytic pathways is known to occur for some compounds, but the environmental significance of this pathway is still imperfectly understood.

General acid/base catalysis is perhaps of less significance in natural fresh waters, although probably of some importance in

special situations. This phenomenon can be described fairly well via the Bronsted law (relating rate constants to pK of general acids and bases) and probably can be incorporated into exposure models in the near future. Maximum rates of general acid/base catalysis can be deduced from a compound's specific acid/base hydrolysis behavior, and actual rates can be determined from relatively simple laboratory experiments (Perdue, Wolfe, and Karickhoff 1981).

A number of cases are known of apparent sediment-catalyzed transformations. These reactions are inhibited by heat sterilization of the system but are unaffected by mercuric chloride or azide bacteriostasis. One possible explanation of this phenomenon involves the presence of exoenzymes activated by attachment to sediment particles. This pathway is in need of considerable additional research if it is to be described in a system-independent way and incorporated into exposure assessment models.

4. Reduction. Reductive dechlorination of organic compounds (e.g., Toxaphene and DDT) in anaerobic soils and sediments has been observed by many investigators (e.g., the summary in Tinsley 1979:92ff). Although the redox state of these systems can be described via redox potential, and pE, the suitability of this thermodynamic quantity as an accurate predictor of environmental kinetics is very uncertain. In

addition, some reductive pathways are catalyzed by ferrous iron. The mechanics, pathways, and kinetics of anaerobic reductions of synthetic organic compounds currently require substantial additional process research. At the moment it is not even clear whether these pathways are intrinsically a biological phenomenon or a chemical phenomenon occurring under reaction conditions produced by the activites of the biota.

Biological Processes

1. Microbial Transformations. Microbial communities are a ubiquitous constitutent of almost all aquatic ecosystems. The microbiota play a central role in the remineralization of plant and animal debris; they have evolved the capacity to transform and harvest energy from an immense array of naturally occurring organic compounds. This ability does not extend to all synthetic compounds, however, and it is now "axiomatic that micro-organisms are fallible and that many synthetic organic compounds are recalcitrant . . . and accumulating in some environments" (Alexander 1979a). In consequence, qualitative "biodegradability" tests (Swisher 1970) are now routine in the detergent industry, and "sludge" tests have been suggested (Buzzell, Thompson, and Ryckman 1969) as a routine procedure for evaluating industrial synthetic organic compounds. The latter tests can also provide some assurance that the compound will not destroy the microbial communities that serve man in sewage treatment plants, as well as providing an evaluation of the

biodegradability of the compound (e.g., Baird et al. 1974).

The discovery of microbial fallibility has led to a more critical and quantitative view of microbial metabolism of synthetic organics; it no longer suffices to know that a compound is "biodegradable." Instead the rates, products, microbial populations, and environmental conditions surrounding an observed biodegradation are of increasing interest to the microbiological and ecological community. Given that the natural microbial substrates can massively accumulate in special circumstances (e.g., peat bogs and swamps), a degree of skepticism is obviously warranted toward any claim of universal, unconditional biodegradability of a synthetic organic compound. The rates at which a compound is biodegraded must depend upon both the structure of the compound and the metabolic capacities of the microbial community resident in the ecosystem receiving the compound.

Microbial communities derive energy for metabolism and growth from the breakdown of organic compounds, and the kinetics of growth and substrate utilization have been of interest to microbiologists for many years. Both population growth and substrate utilization rate have been described via Monod's (1942) analogy with Michaelis-Menten enzyme kinetics (Slater 1979). In this approach, the growth of a microbial population in an unlimiting environment is described by:

$$dN/dt = u\,N$$

where u is called the "specific growth rate" and N is microbial biomass or population size. The Monod equation modifies this formulation via the recognition that consumption of resources in a finite environment must at some point curtail the rate of increase (dN/dt) of the population. This modification is implemented via:

$$u = u(max)\ \frac{[S]}{Ks + [S]}$$

in which [S] is the concentration of the growth limiting substrate, u(max) is the "maximum specific growth rate" obtaining when [S] is present in excess (i.e., non-limiting), and Ks, the "saturation constant" is that value of [S] allowing the population to grow at rate u(max)/2. An equation describing the behavior of the growth substrate [S] over time, and thus by implication the dynamics of a biodegradable synthetic compound, follows via a simple derivation (Slater 1979): Assuming that a fixed amount of growth results from metabolism (and therefore loss from solution) of a unit quantity of S, then

$$dN = -Y\,dS$$

where Y is the "yield coefficient" in cells or biomass produced per unit S metabolized. Taking

$$\frac{dS}{dt} = \frac{dS}{dN}\,\frac{dN}{dt}$$

gives

$$dS/dt = -(u/Y)\,N$$

or, substituting $u(max)[S]/(Ks + [S])$ for u,

$$\frac{dS}{dt} = -\frac{u(max)}{Y}\,\frac{[S]}{Ks + [S]}\,N$$

The observed microbial growth yield Y is often calculated from the amount of microbial biomass produced during the course of transformation of a measured quantity of substrate. Because a microbial population must satisfy maintenance requirements before any growth can occur, the apparent yield Y can fall quite drastically at low concentrations of S. Expressions with separated growth and maintenance yields have been developed (Pirt 1975), and it is possible to compute the separate magnitudes of growth and maintenance yields from microbial growth experiments (Slater 1979).

The Monod formulation has been successfully applied to biotransformation of synthetic chemicals in a laboratory setting. These studies have demonstrated that a Monod analysis need not be restricted to single-species populations, that is, the Monod equations can serve as adequate descriptors of substrate transformation by "mixed" or "heterogeneous" (i.e. multi-species) microbial populations. In one example, Paris,

Lewis, and Wolfe (1975) isolated a 4-species consortium of organisms able to use malathion as its sole source of carbon. Analysis of the growth response of the population and of concurrent malathion transformation rates then gave the Monod parameters u(max) = 0.37 /hr, Ks = 2.17 uM/L (0.716 mg/L), and Y = 4.1E10 cells/uM (1.2E11 cells/mg). In a similar study, Smith and coworkers (1978) investigated the degradation of p-cresol by mixed microbial cultures able to use the compound as a sole carbon source. These authors expressed their results in terms of Monod parameters, finding u(max) = 0.62 /hr, Y = 1.8E9 cells/mg, and Ks = 0.84 mg/L.

Unfortunately, these elegant applications of classical microbiological methods to the biotransformation or "biolysis" of synthetic organic compounds are difficult to apply in a broader ecological context. The first difficulty, which has received some attention in the microbiological literature, is primarily mechanical: The Monod formulation is non-linear in its parameters and, thus, imposes a high cost in computation time when used in a computer program or mathematical model. For trace concentrations of pollutants (i.e. [S] << Ks), however, the term (Ks + [S]) in the denominator of the Monod equation can be approximated by Ks, giving the linear approximation:

$$\frac{d[S]}{dt} = - \frac{u(max)}{Y\ Ks} N\ [S]$$

This formulation is similar to the "second-order" equations used

to describe the kinetics of chemical reactions, and the term u(max)/(Y*Ks) can be termed, by analogy, a second-order biolysis rate constant Kb2, with units /hr/(cells/L) when population sizes N are expressed in cells/L.

The propriety of this substitution can be readily evaluated. For malathion, u(max)/(Y*Ks) = 0.37/(4.1E10*2.17) = 4.16E-12 /hr/(cells/L). Paris et al. (1975) also computed values of Kb2 from microbial population sizes and malathion transformation rates in their experimental studies, finding a mean value for Kb2 of (2.6+0.7)E-12 (95% confidence interval) /hr/(cells/L) for a series of 8 experimental determinations spanning a concentration range from 0.0273 to 0.33 uM in malathion. The measured Kb2 differed from u(max)/(Y*Ks) by less than a factor of 2, suggesting that simplified kinetic experiments could be used to develop second-order rate constants, in lieu of a detailed elaboration of u(max), Y, and Ks, when the region of concern is restricted to levels of compound << Ks.

Furthermore, dissolved pesticide concentrations in surface waters are often very low indeed. For example, dieldrin, lindane, and DDT have been found primarily at ng/L levels both in the USA (Matsumura 1972) and in Britain (Brooks 1972). For industrial chemicals, however, the situation can be somewhat different. For example, the release of phenolic wastes into the St. Lawrence River results in riverine concentrations of 0.01 to

0.15 mg/L (Visser et al. 1977). Although these high concentrations are restricted to a dispersion cone immediately downstream of the effluents, Ks for p-cresol (0.84 mg/L) is uncomfortably close to the highest measured concentrations.

The need for a thorough evaluation of the adequacy of a linear approximation to the Monod formula disappears, however, upon examination of the conceptual difficulties standing in the way of the application of either equation to environmental situations. A natural microbial community derives its energy from a large variety of organic detrital materials. A microbial species restricted to a trace-level synthetic compound as its sole carbon source would be at a severe competitive disadvantage; there is no way of predicting a priori the population densities the degrader could attain in real systems. Even when a synthetic compound is sufficiently similar to natural substrates that it can be indifferently degraded by the microbial community as a whole, the presence of multiple energy-yielding substrates in the environment violates a fundamental assumption underlying the Monod approach, that is, that [S], the synthetic compound, limits growth. In many instances, moreover, a compound may be transformed or degraded in an energy-requiring detoxification process, making the concept of cell yield (Y) of dubious utility. When the compound, for whatever reason, is degraded in the absence of a change in population size, the apparent zero yield forces abandonment of either version of the Monod equation.

(This phenomenon is sometimes called "cometabolism," e.g., Alexander 1979b; Jacobson, O'Mara, and Alexander 1980.)

Despite these difficulties, the rate of transformation of organic pollutants must depend on the structure of the compound and the metabolic capacity of microbial communities. The simplest expression of this duality is the second-order equation:

$$d[S]/dt = - Kb2\ B\ [S]$$

which asserts that the rate of biolysis (d[S]/dt) is first-order in compound concentration [S] and in microbial activity B, and in which the identification of Kb2 with u(max)/(Y*Ks) is discarded. This approach requires that the second-order rate constant be determined via laboratory studies of relatively undisturbed samples drawn from natural microbial communities. It also requires demonstration that d[S]/dt is linearly proportional to [S] for fixed levels of B, and that appropriate measures of B be found.

One conventional microbiological technique for characterizing microbial populations is simple population size, measured, for example, by colony counts on pour-plate agars (APHA 1976). To the extent that population size is an adequate measure of community metabolic capacity, simple microbiological techniques could serve to characterize the rate of

biotransformation of synthetic compounds in natural environments. This hypothesis has been explored for three compounds (butoxyethyl ester of 2,4-D (2,4-DBE), malathion, and chlorpropham) by Paris and coworkers (Baughman, Paris, and Steen 1980; Paris et al. 1981). These authors investigated biotransformation of their study compounds in samples of natural waters drawn from 40 locations in the continental USA. Ambient water temperatures at the collection points ranged from 1 to 29 degrees C, and the laboratory studies were conducted at the observed ambient temperature of the sampled environments. Ambient bacterial populations, as measured by 48-hour incubation on TGE (tryptone glucose extract) agar at 22 degrees C, ranged from 4.E2 to 9.E5 cells/ml (Paris et al. 1981). Biolysis of these chemicals was demonstrably first-order in compound concentration and in population size (Fig. 2) and was relatively independent of temperature. The 95% confidence intervals (based on between-site variation) for Kb2 (/hr/(cell/L)) and number of sites for these compounds were (5.42+0.97)E-10 (2,4-DBE, 31 sites), (4.54+0.74)E-11 (malathion, 14 sites), and (2.63+0.72) E-14 (chlorpropham, 11 sites).

Evaluation of biolysis in such "river die-away" studies is particularly difficult when a combination of small populations and slow rates of biotransformation leads to inconveniently long biolysis halflives. In such cases population densities must be augmented via centrifugation or supplemental nutrient broth. The

latter procedure can have the disadvantage of favoring opportunistic heterotrophs at the expense of organisms better equipped to degrade more recalcitrant compounds. For example, the second-order biolysis rate constant (Kb2) for chlorpropham is unaffected when population densities are augmented via nutrient broth supplementation, but the measured Kb2 for phenanthrene decreases in approximate proportion with the the population increase (Paris, oral comm.).

Steen, Baughman, and Paris, (1980) reported second-order rate constants for aerobic biotransformation of synthetic chemicals by microbial populations derived from aquatic sediments. The observed rate constants for 2,4-DBE and malathion were consistent with the rate of degradation by water-column populations, at Kb2 of 2.3E-10 and 4.0E-11 /hr/(cell/L), respectively. Aerobic biolysis of chlorpropham by the sediment-derived populations, however, was almost an order of magnitude faster (Kb2 = 1.42E-13) than biolysis by the water-column populations (Kb2 = 2.4E-14 /hr/(cell/L)). By varying the sediment/water ratio, these authors also adduced evidence suggesting that chlorpropham, methoxychlor, and several phthalate esters, when sorbed to suspended sediments, became relatively unavailable to biolytic organisms.

Plate-count estimates of bacterial population densities are extremely selective and may in some circumstances underestimate

total population sizes by 3 or more orders of magnitude (Wetzel 1975:571, Fletcher 1979, Jannasch and Jones 1959). Furthermore, although increases in pollutant flux (i.e., ng/L/time or mass reacted/time) with increasing chemical concentration (consonant with pseudo-first-order kinetics) have been observed in nature (e.g., Sherrill and Sayler 1980), it is also true that, at elevated pollutant concentrations, both a reduction in the apparent first-order rate constant (Tinsley 1979:149ff), and zero-order kinetics (Visser et al. 1977) have been observed. The latter phenomena are consonant (mathematically) with a Monod formulation. It is not clear, however, whether these kinetics are a reflection of the maximum growth rate of a specialized sub-population of degraders or result from toxic effects of elevated concentrations on the microbial community.

In any case, it is clear that the studies of second-order kinetics cited above are a useful beginning in the detailed quantitative study of rates of biotransformation of pollutant chemicals. Little more extrapolative power can be developed until such time as the mechanisms of biotransformations, and the environmental coupling variables that govern the metabolic capacity of natural and laboratory microbial populations, have been rigorously determined and measured in both kinds of systems. Presumably metabolic capacity is related to the nutrient status of the cells, which in turn is related to the nutrient history of the water-body. Functional descriptions of these relationships

are an important subject for additional research. Furthermore, some compounds are degraded only by specific subpopulations of the natural microbial community. Although the second-order rate constant describing the biolysis capacity of specific transforming species is insensitive to the growth phase of the population (Fig. 3), it is not currently possible to predict the population density of functional subpopulations in natural communities. Finally, the in situ biolysis capacities of sediment microbial populations have not been fully characterized; fungi, aerobic bacteria, and anaerobes may play important roles in benthic subsystems.

2. Algal Transformations. Little can be said about algal metabolism of synthetic organics beyond the simple observation that the phenomenon is known to occur (e.g., O'Kelley and Deason 1976). The biolysis capacity of algae, its relationship to photosynthetic rates or light intensities, nutrient status, and other presumptive influences on this pathway, are all open areas for process-level research. Although perhaps of relatively slight significance to the overall fate of most compounds, algal degradation may in effect limit the degree of food-chain transmission of pollutants in some cases.

3. Biosorption and bioaccumulation. Although perhaps somewhat beyond the scope of this discussion, the transfer of synthetic organics to living organisms deserves at least passing

mention. In most cases, the biota constitutes a sufficiently small fraction of the total volume of the system that the total mass of chemical associated with it is negligible. In a total mass balance sense, then, transport vectors (e.g., fish migration, diel vertical migration of zooplankton) usually have little effect on the overall dynamics of a synthetic organic pollutant. Still, transfer of pollutants up the food chain, and direct pollutant transfer to otherwise uncontaminated populations (e.g., human consumption of contaminated fishes), suggest that this topic should not be altogether neglected in discussions of aquatic fate models. In the case of microorganisms, with their very high surface to volume ratio, capture of synthetic organics can be described via a simple partition coefficient (Baughman and Paris 1981). Simple partitioning probably can be used to describe equilibrium uptake of synthetic organics by the vast majority of organisms occupying the base of aquatic food chains. The uptake of pollutant chemicals by higher organisms is complicated by the presence of multiple dietary and direct routes of exposure, including transport across gill membranes and, at least for marine fishes, direct water intake. Clearly the significance of partitioning phenomena, as against dietary uptake, must differ with the physiology and life history of the individual type of organism affected. For example, blue crabs (Callinectes) appear to take up little or no Kepone via direct absorption from seawater, but readily accumulate this compound via dietary intake (Schimmel et al. 1979). Although simple

biosorption or bioconcentration factors are adequate for many purposes, detailed exposure models probably should include a capability for representing dietary exposures, biosorption or membrane transfers, and depuration kinetics in at least a generalized sense. Some effort has been devoted to a "bioenergetic" dietary model (Weininger 1978). The logic of this approach is similar to that used for human exposures; it holds considerable promise for inclusion in exposure models.

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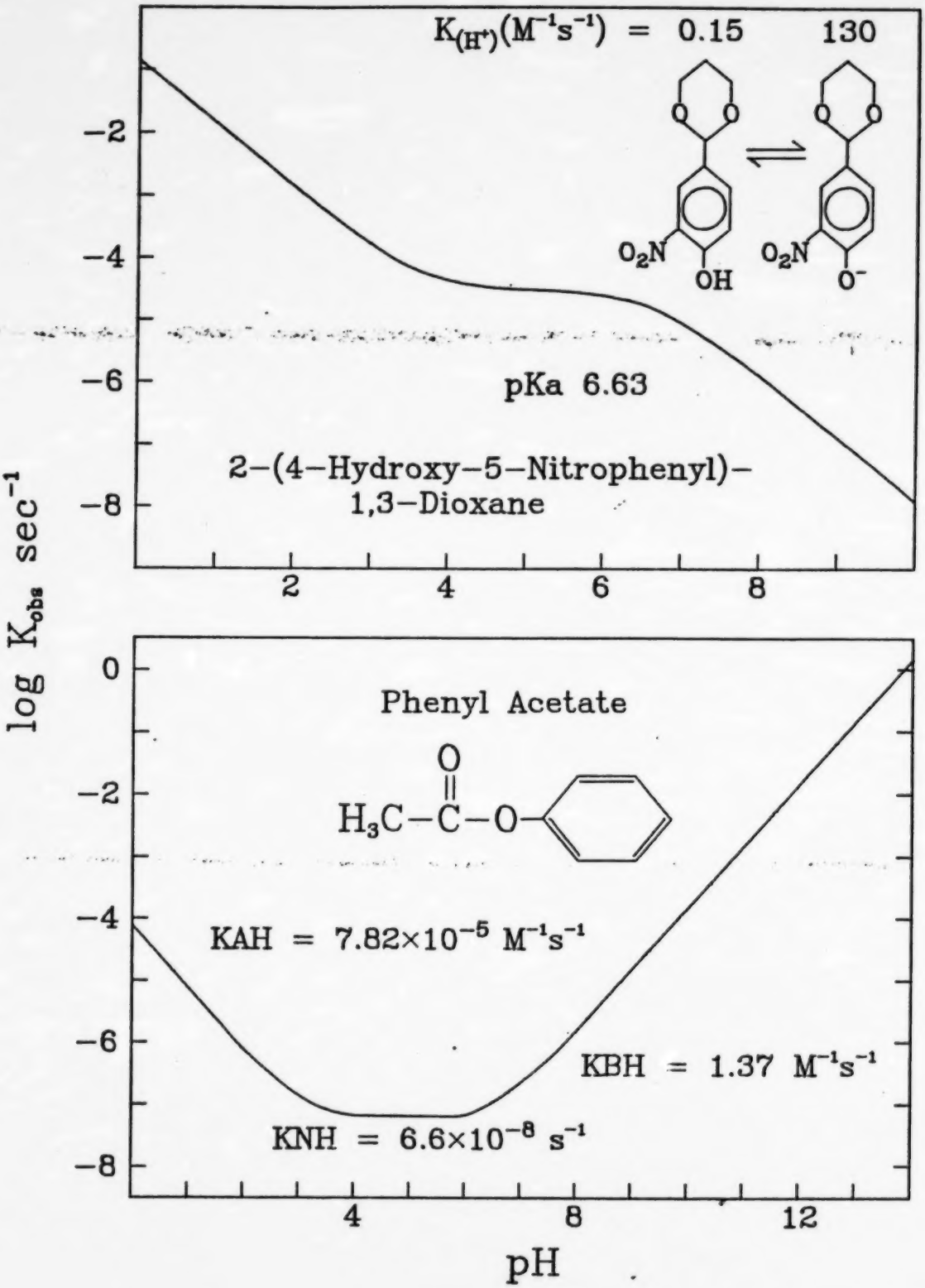
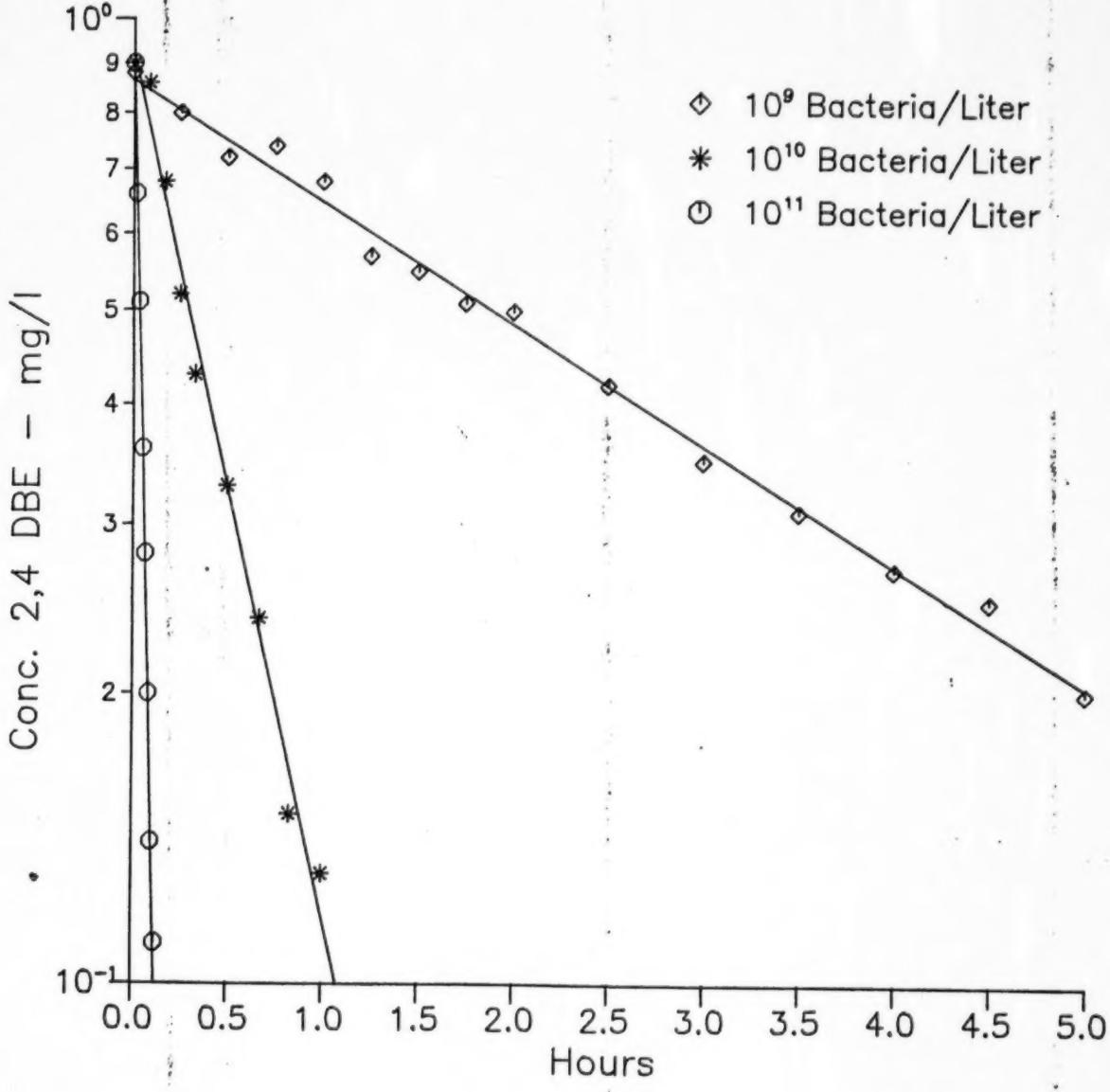
Figure Captions

1. Hydrolysis pH-rate profiles of phenyl acetate (lower) and a substituted 2-phenyl-1,3-dioxane (HND). Phenyl acetate profile constructed from data of Mabey and Mill 1978, HND profile from data of Bender and Silver 1963. Phenyl acetate reacts via specific-acid catalyzed, neutral, and base-catalyzed transformation pathways. HND hydrolyzes only via an acid-catalyzed pathway; the phenolate anion is some 867 times more reactive than its conjugate acid.

2. Microbial transformation kinetics of butoxyethyl ester of 2,4-dichlorophenoxyacetic acid (2,4 DBE). Bacterial populations from Overlook Lake, Georgia; population densities measured via 48 hr incubations at 22 degrees C on tryptone glucose extract (TGE) agar. (From Paris et al. 1981.)

3. Time course of transformation of methyl parathion by Flavobacterium aquatile in nutrient broth during a variety of growth phases of the experimental population. Note relative stability of the second-order biolysis rate constant. Figure supplied courtesy of D.L. Lewis (unpublished observations).


$K_{(H^+)}(M^{-1}s^{-1})$ = 0.15 130
pKa 6.63
2-(4-Hydroxy-5-Nitrophenyl)-
1,3-Dioxane
Phenyl Acetate
KAH = 7.82×10^{-5} $M^{-1}s^{-1}$
KBH = 1.37 $M^{-1}s^{-1}$
KNH = 6.6×10^{-8} s^{-1}
log K_{obs} sec^{-1}
pH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Conc. 2,4 DBE – mg/l
0.0
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3.5
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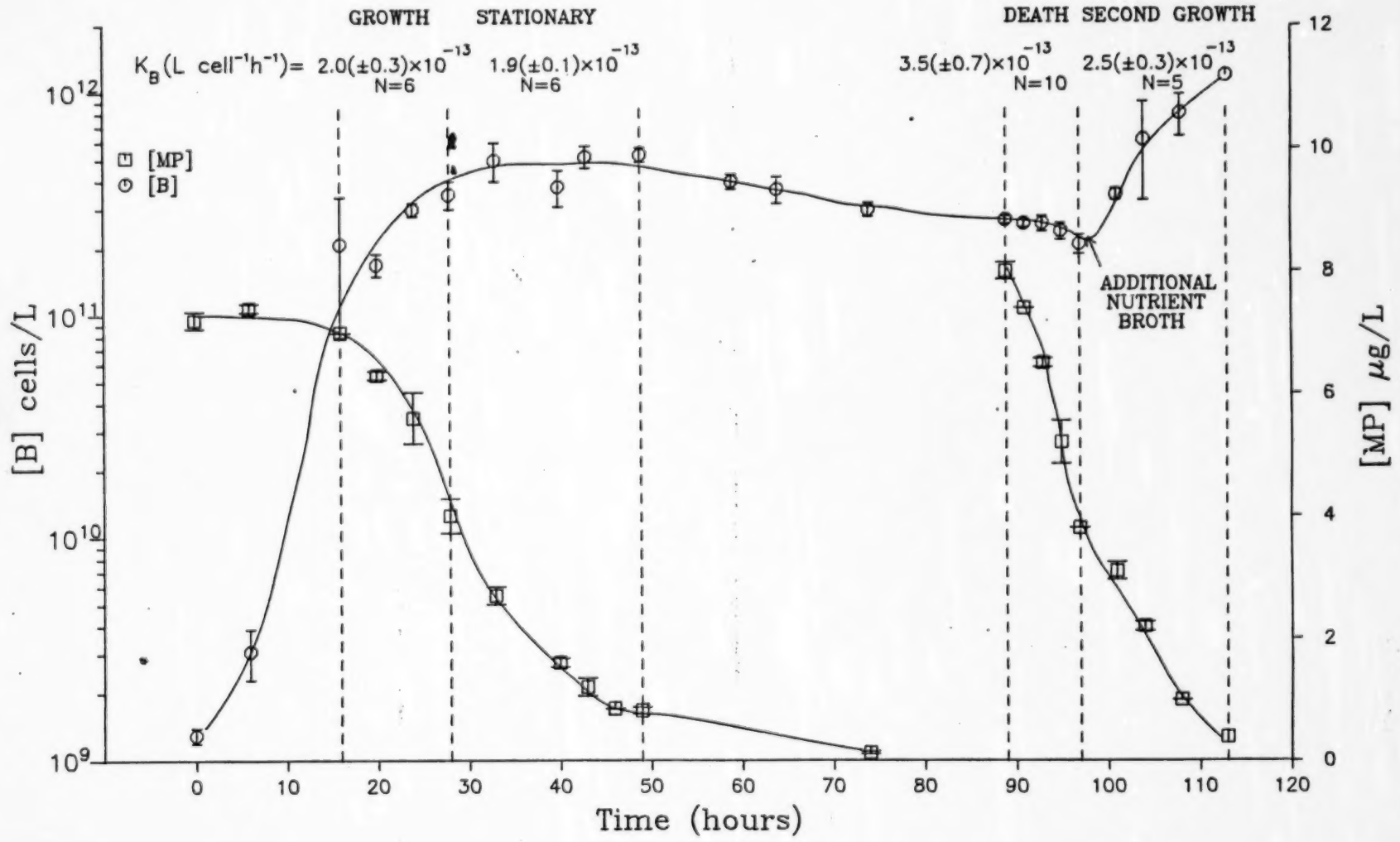
Hours
10^9 Bacteria/Liter
10^{10} Bacteria/Liter
10^{11} Bacteria/Liter


GROWTH
STATIONARY
DEATH
SECOND GROWTH
K_B(L cell^{-1}h^{-1})= 2.0(±0.3)×10^{-13} N=6
1.9(±0.1)×10^{-13} N=6
3.5(±0.7)×10^{-13} N=10
2.5(±0.3)×10^{-13} N=5
[MP]
[B]
ADDITIONAL NUTRIENT BROTH
[B] cells/L
[MP] μg/L
Time (hours)